

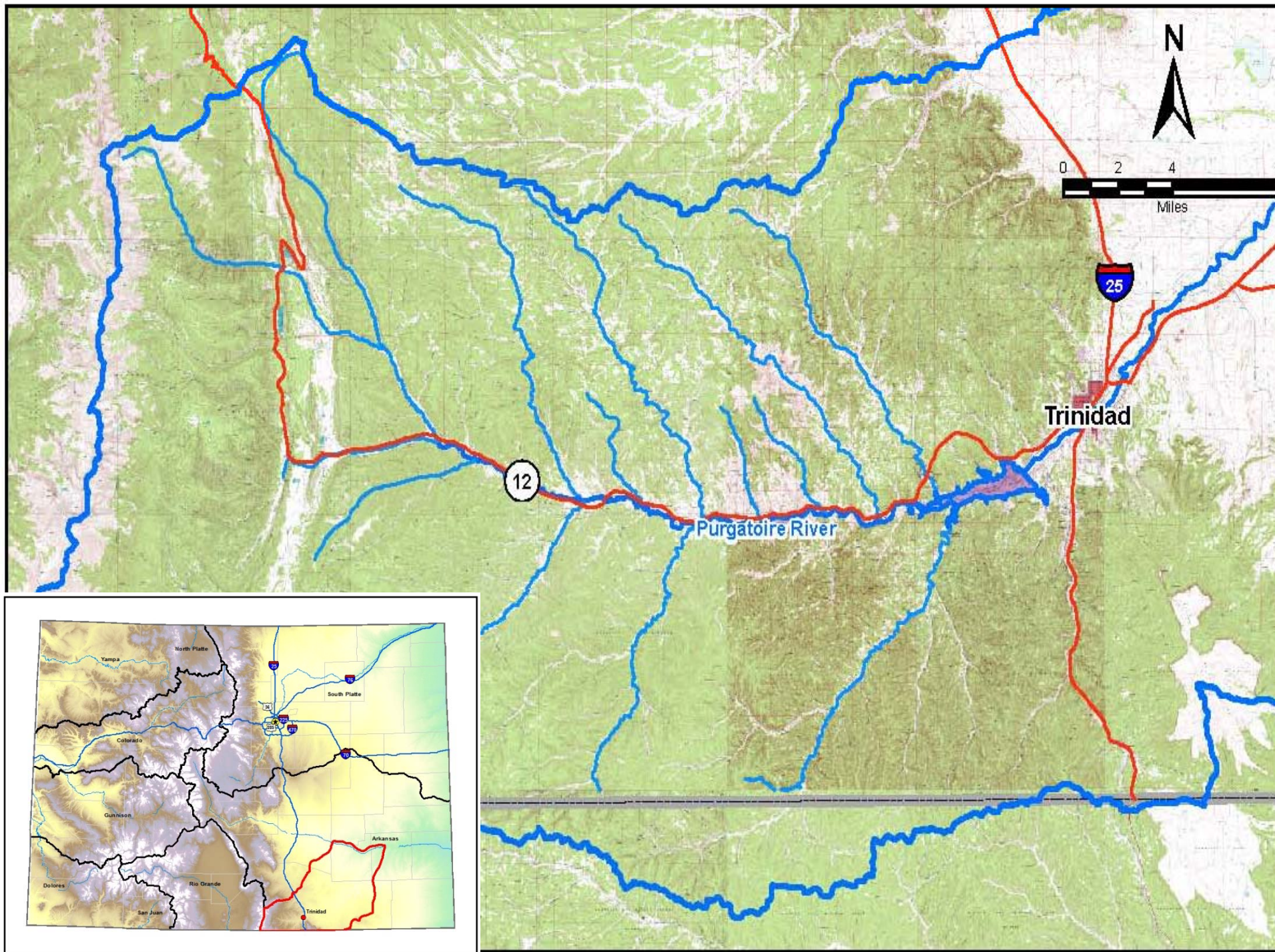
Whole effluent toxicity (WET) / Alternative testing procedure (ATP) Meeting

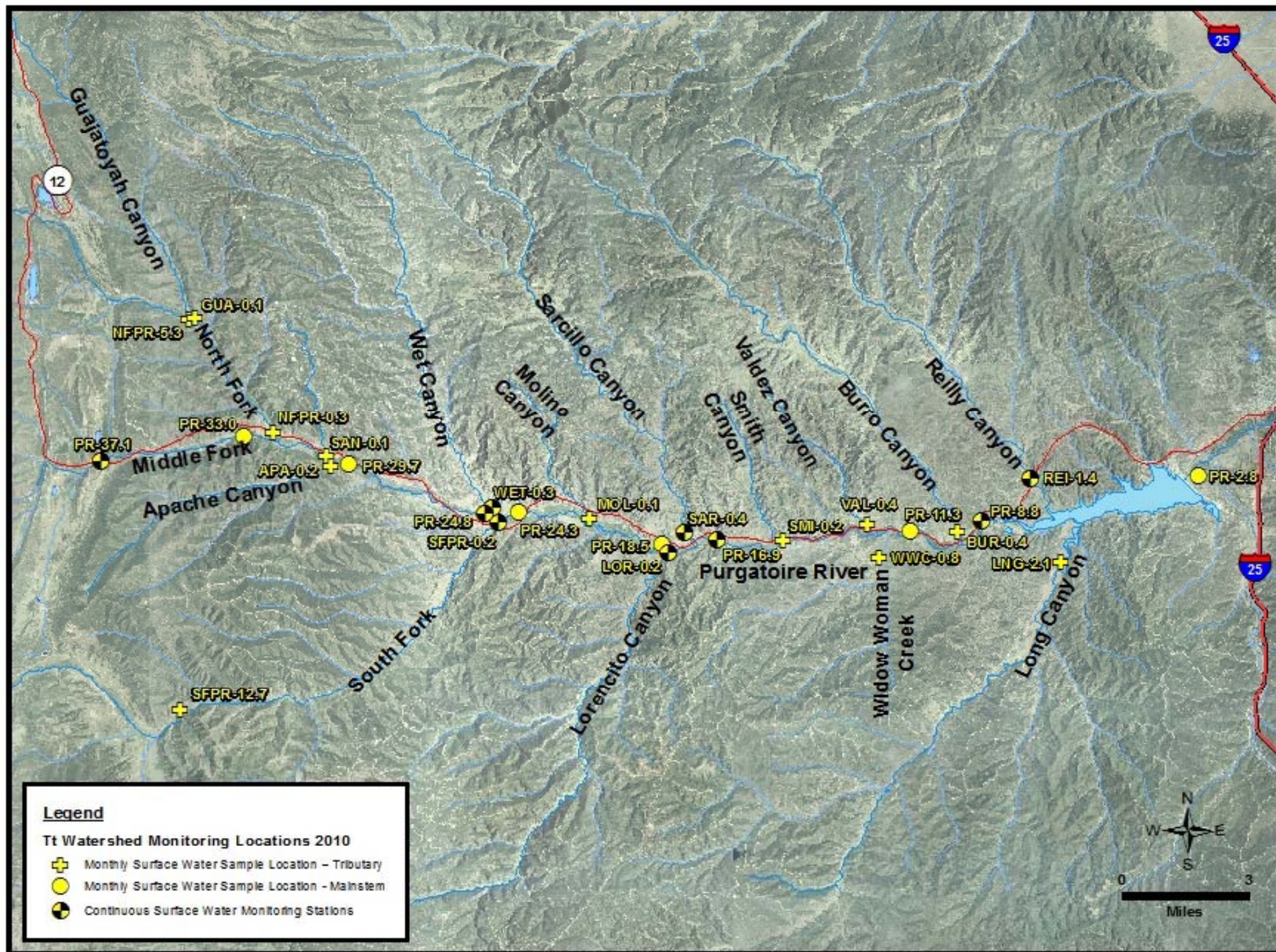
Raton Basin Watershed
(PNR & XTO)

Objective

- Investigate the opportunity to substitute short-term chronic WET test organism (invertebrate *Ceriodaphnia dubia*) with an alternative test organism / method for testing in the Raton Basin Watershed while still being protective of aquatic species

Overview of Coal Bed Natural Gas processes in Raton Basin





Monthly Monitoring Analyte List

Analyte Group	Constituent	Method Number	Sample Preservation and Treatment	Holding Times
Field Parameters	pH	EPA 150.1	Measure In-Situ	Immediately
	Specific Conductance	EPA 120.1		28 days
	Temperature	EPA 170.1		Immediately
Metals	Boron ^{D,T}	EPA 200.7 ICP	Acidify with HNO ₃ ; pH <2	6 months
	Calcium ^D	EPA 200.7 ICP	Acidify with HNO ₃ ; pH <2	6 months
	Copper ^{D,PD,TR}	EPA 200.8 ICP-MS	Acidify with HNO ₃ ; pH <2	6 months
	Iron ^{D,TR}	EPA 200.7 ICP	Acidify with HNO ₃ ; pH <2	6 months
	Lead ^{D,PD,TR}	EPA 200.8 ICP-MS	Acidify with HNO ₃ ; pH <2	6 months
	Magnesium ^D	EPA 200.7 ICP	Acidify with HNO ₃ ; pH <2	6 months
	Potassium ^D	EPA 200.7 ICP	Acidify with HNO ₃ ; pH <2	6 months
	Selenium ^{D,PD,TR}	EPA 200.8 ICP-MS	Acidify with HNO ₃ ; pH <2	6 months
	Sodium ^D	EPA 200.7 ICP	Acidify with HNO ₃ ; pH <2	6 months
	Zinc ^{D,PD,TR}	EPA 200.7 ICP	Acidify with HNO ₃ ; pH <2	6 months
Wet Chemistry	Alkalinity	SM2320B - Titration	Chill to 4 degrees C	14 days
	Chloride	SM4500Cl-E	Chill to 4 degrees C	28 days
	Sulfate	EPA 375.4 - Turbidimetric	Chill to 4 degrees C	28 days
	Total Suspended Solids (TSS)	SM2540D	Chill to 4 degrees C	7 days
	Total Dissolved Solids (TDS)	SM2540C	Chill to 4 degrees C	7 days

Notes:

D = Dissolved form.

PD = Potentially dissolved form.

TR = Total recoverable form.

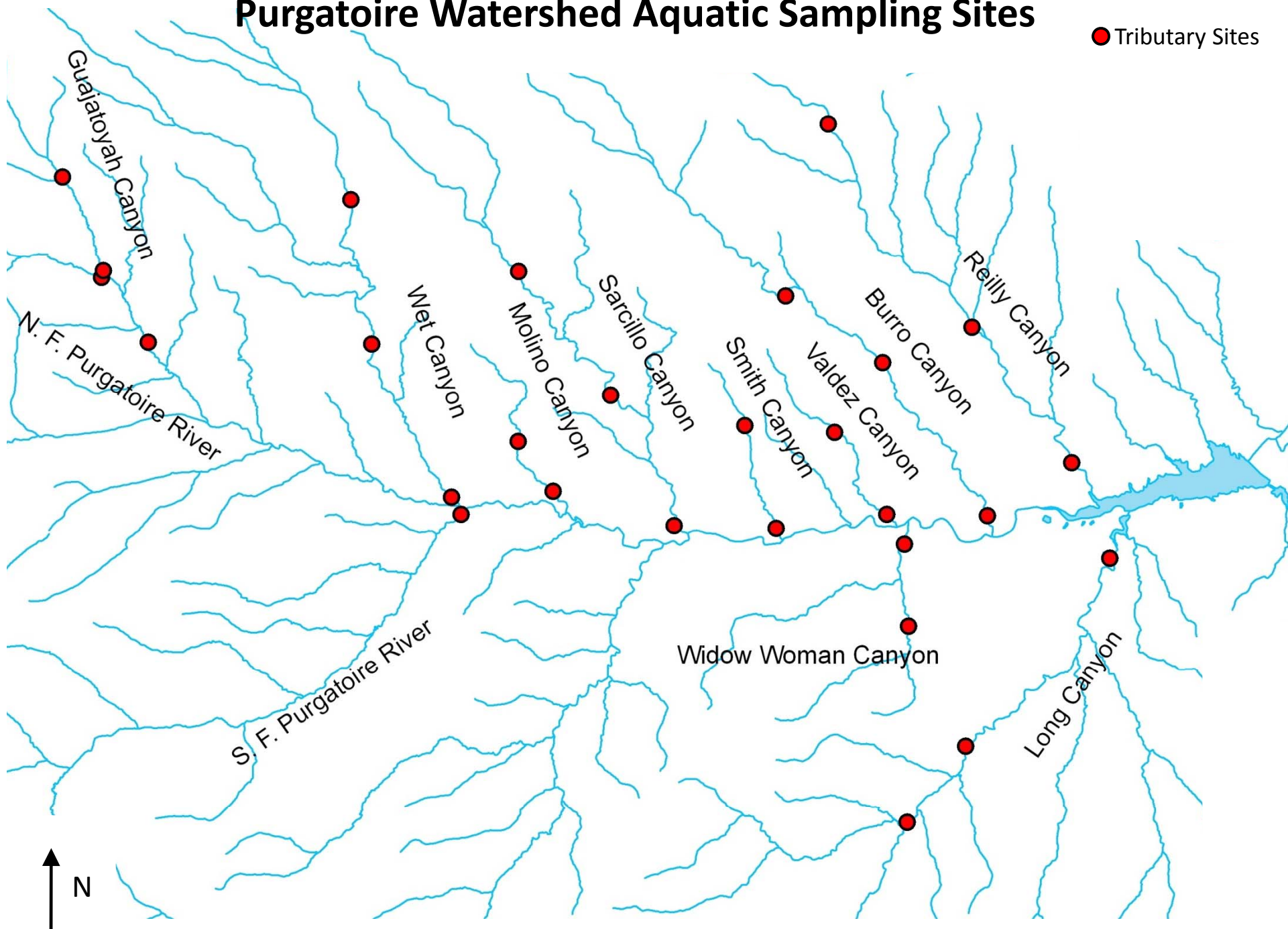
T = Total form.

EPA = U.S. Environmental Protection Agency

SM = Standard Methods (AWWA)

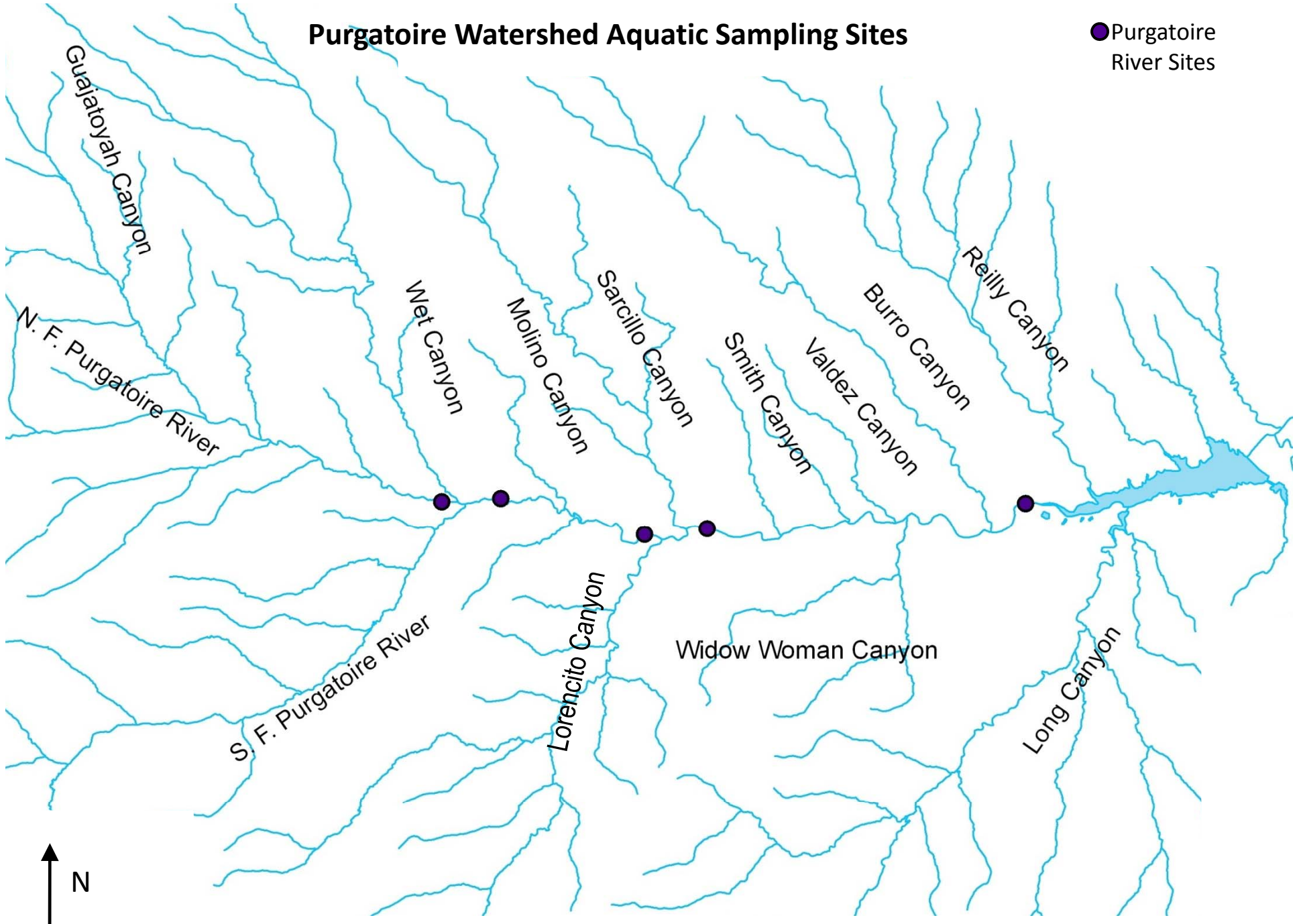
Purgatoire Watershed Aquatic Sampling Sites

● Tributary Sites



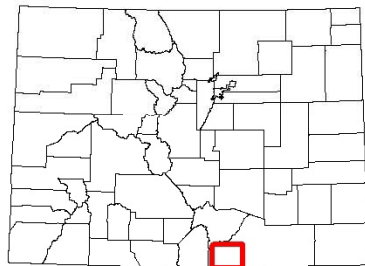
Purgatoire Watershed Aquatic Sampling Sites

● Purgatoire
River Sites



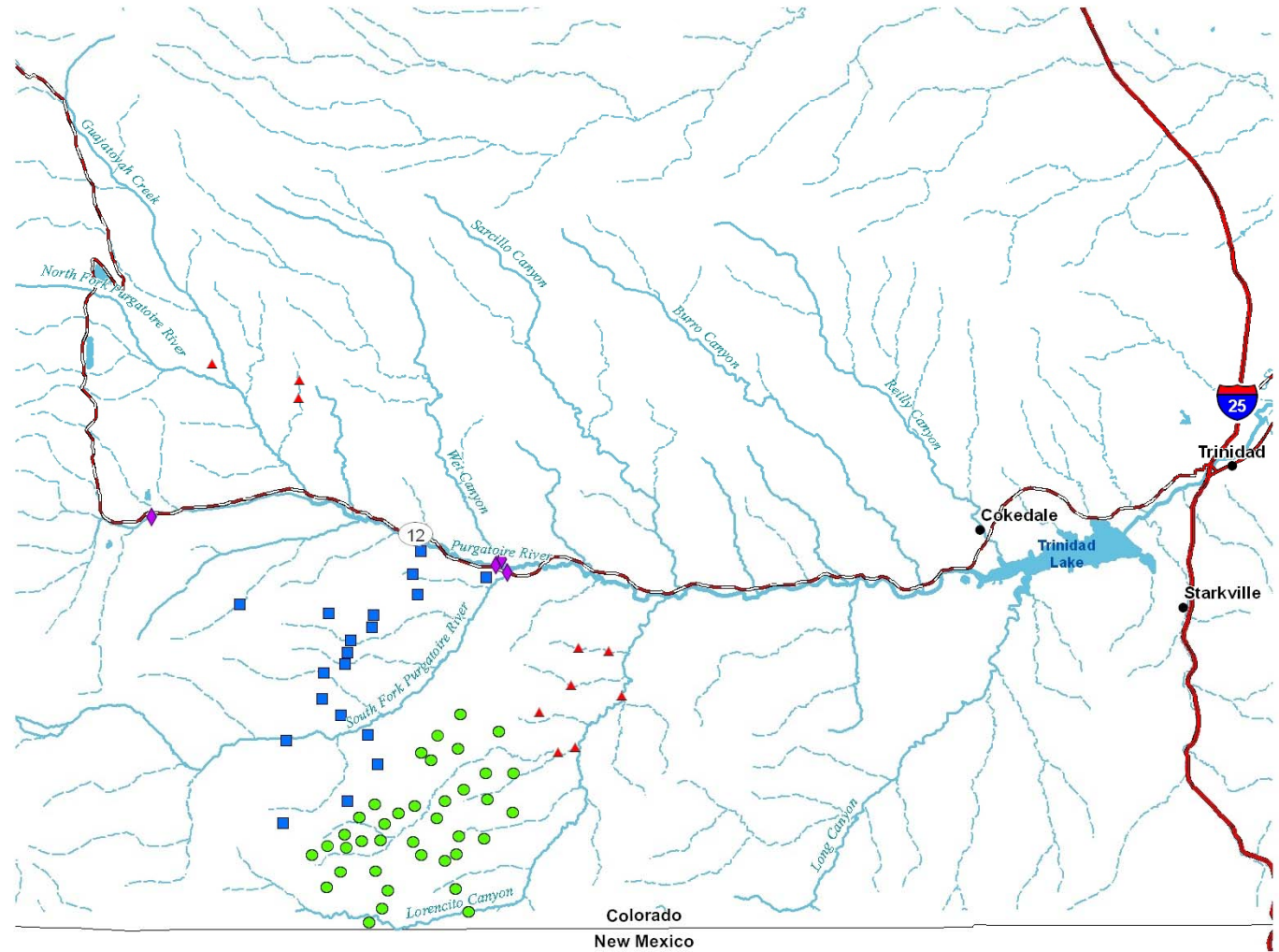
XTO & PNR Outfalls with chronic WET

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Legend

- ▲ PNR Site
- XTO 54 Site
- XTO 62 Site
- ◆ XTO PR Site



0 2.5 5
Miles
1:300,000

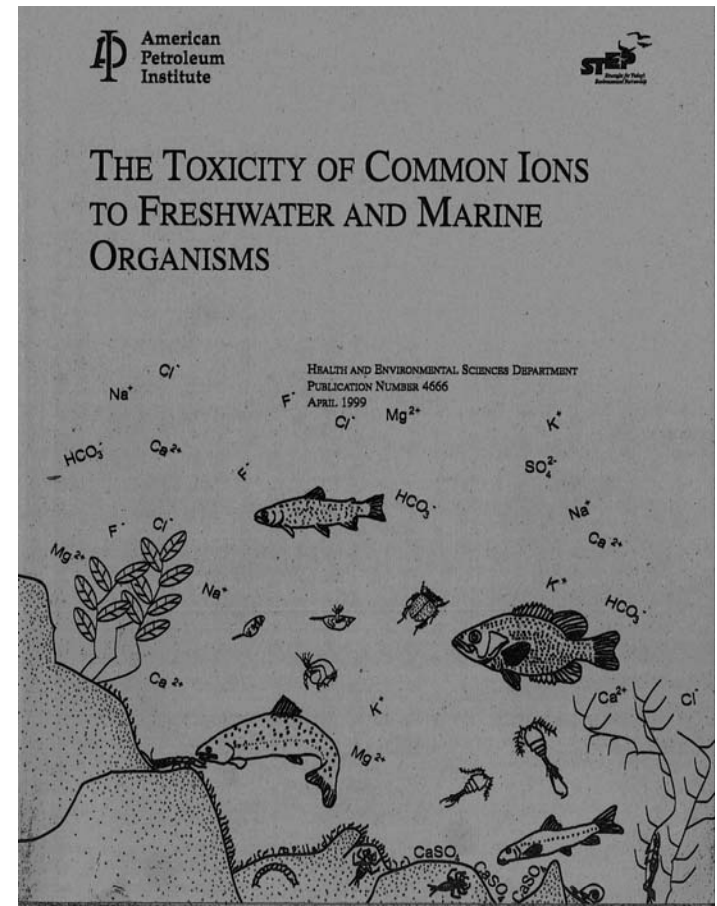


Working Hypothesis

- The toxicity observed in WET tests with *C. dubia* in this watershed is related to total dissolved solids (TDS)
- Question: Given that *C. dubia* are known to be sensitive to TDS ions would another test species (e.g., *Daphnia magna*) be a suitable replacement species in this watershed and still be protective of other aquatic species?

Total dissolved solids

- TDS toxicity in freshwaters
 - Must look at the individual ion concentrations
- Freshwater: 7 major ions
 - Cations
 - Ca^{2+} , Mg^{2+} , K^+ , Na^+
 - Anions
 - Cl^- , HCO_3^- , SO_4^{2-}
- Sources of information
 - API publication (at right)
 - GRI FW STR model
 - Goodfellow et al. 2000 *Environ Toxicol Chem*



Freshwater test organisms



L to R
Daphnia magna
D. pulex
Ceriodaphnia dubia

Fathead minnow larvae
(*Pimephales promelas*)



Fresh water WET methods

- Acute methods (24-96-hrs)
 - Monitor lethal effects to effluents
 - Invertebrates (*C. dubia*, *D. pulex*, *D. magna*)
 - Vertebrate (*P. promelas*, *O. mykiss*)
- Short term chronic (STC) methods (4-8 d)
 - Monitor lethal and sublethal effects to effluents
 - Invertebrate
 - *C. dubia* 3-brood survival and reproduction study
 - Vertebrate
 - 7-d *P. promelas* survival and growth study
 - Plant
 - 96-h algal growth study
 - » *Pseudokirchneriella subcapitata* (at right)



Comparison of Invertebrate STC Methods

3-brood *C. dubia* test

- Duration: 6-8 days
- Organisms per chamber: 1
- Volume: 15 ml
- Reps: 10
- Temp: 25°C
- Food: 0.2 ml 1:1 algae & YCT
 - Algae (10^6 cells/ml)
- Criteria: >80% survival, 15 avg yng, 60% of cntrls must have 3 broods, PMSD (13-48)
- Endpts: survival and repro

USEPA 2002

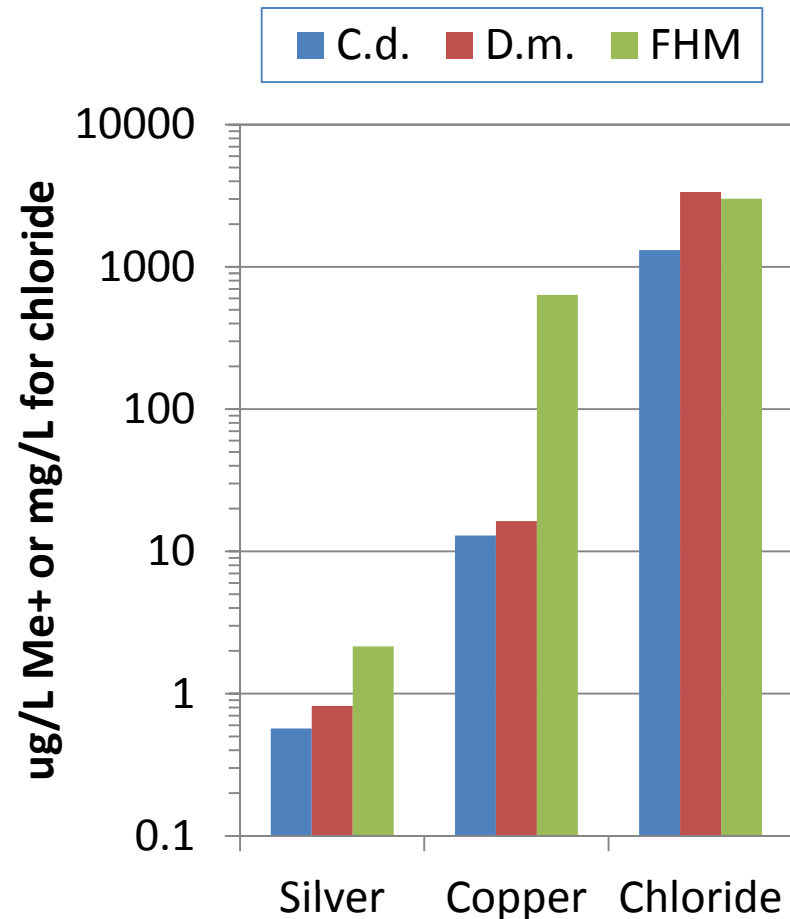
4-d *D. magna* test

- Duration: 4 days
- Organisms per chamber: 5
- Volume: 50 ml
- Reps: 4
- Temp: 25°C
- Food: 0.5 ml 3:2 algae & WG (C)
 - Algae (10^8 cells/ml)
- Criteria: >90% survival, 10X growth from pre wts
- Endpts: survival and dwt

Lazorchak et al. 2009

Relative acute sensitivity of FW species

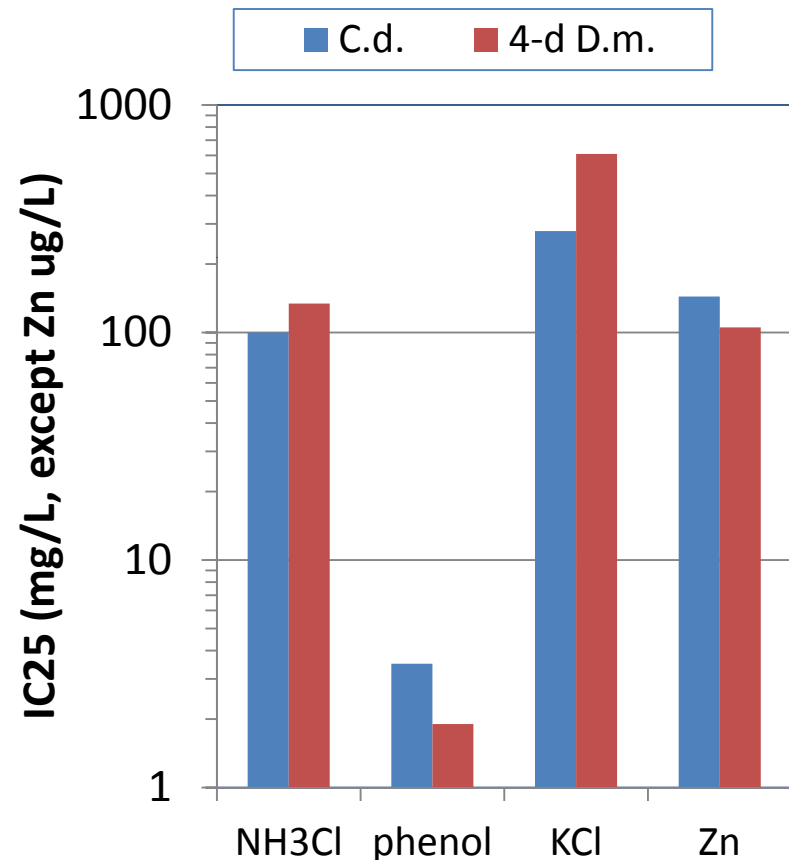
- *C. dubia*
 - one of most common aquatic test organisms
 - sensitive
- *D. magna*
 - relatively sensitive
 - tolerant of TDS ions
 - no promulgated STC mtd (chronic is 21 d)
- FHMs
 - standard aquatic vertebrate test species
 - less sensitive than inverts
 - exceptions include NH_3 , sulfide



Data from AECOM

Comparison STC toxicity of methods

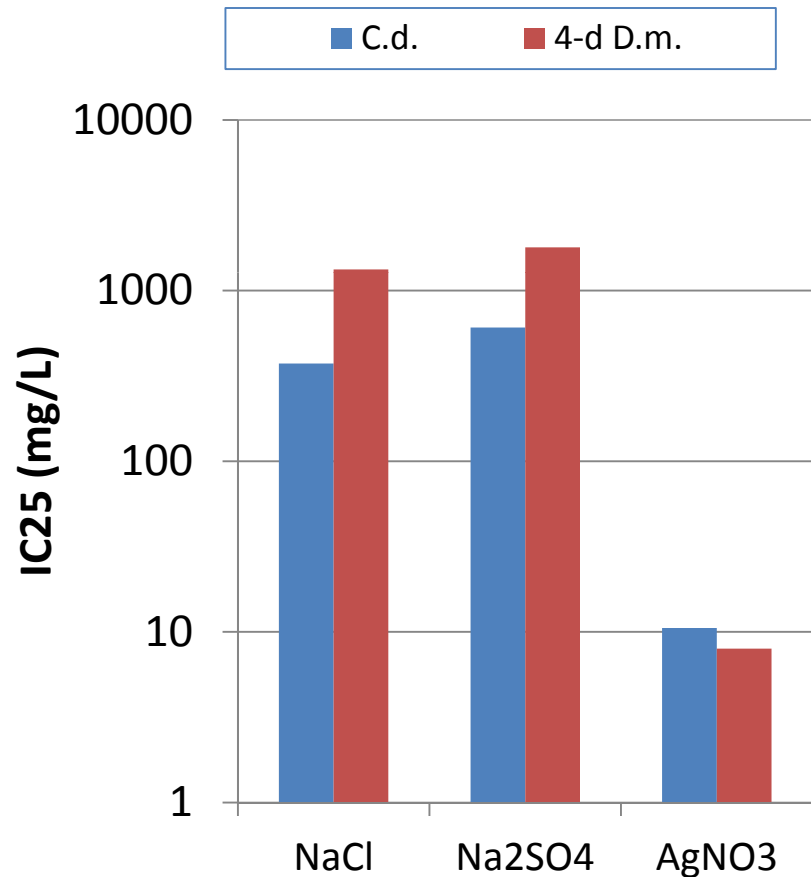
- Lazorchak et al. 2009
- Studies performed to compare STC toxicity of different toxicants using two methods
 - *C. dubia* STC
 - *D. magna* (4-d)
- Similar sensitivity of methods



Data from Lazorchak et al. 2009

Relative short-term chronic toxicity

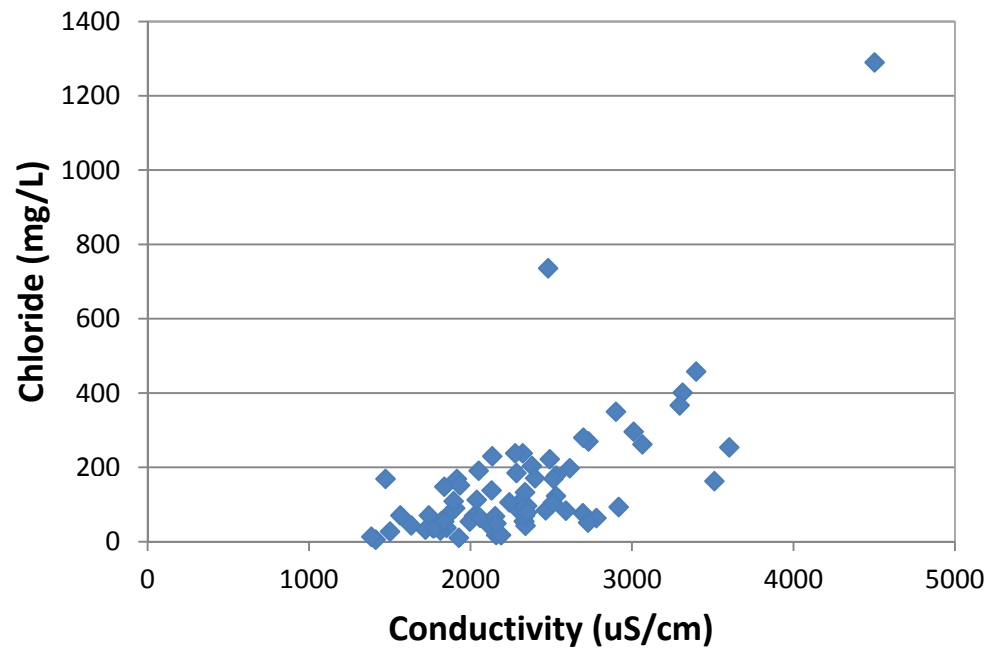
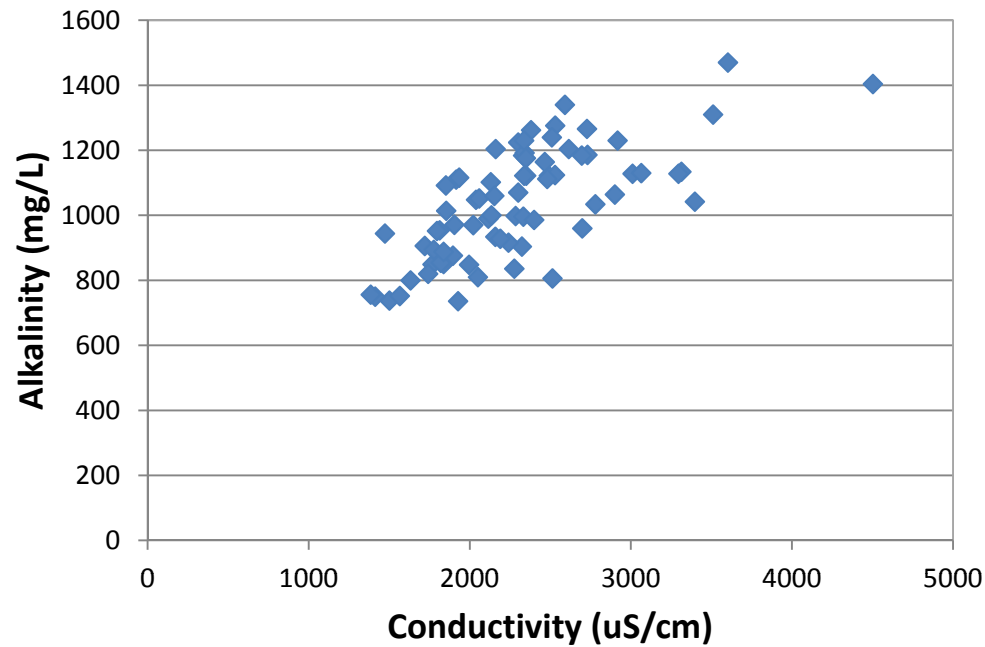
- Studies were performed to compare STC toxicity
 - *C. dubia*
 - *D. magna* (4-d)
- *D. magna* more tolerant of chloride and sulfate than *C. dubia*
- Relative anion toxicity to *C. dubia*
 - $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$
- Similar sensitivity to Ag



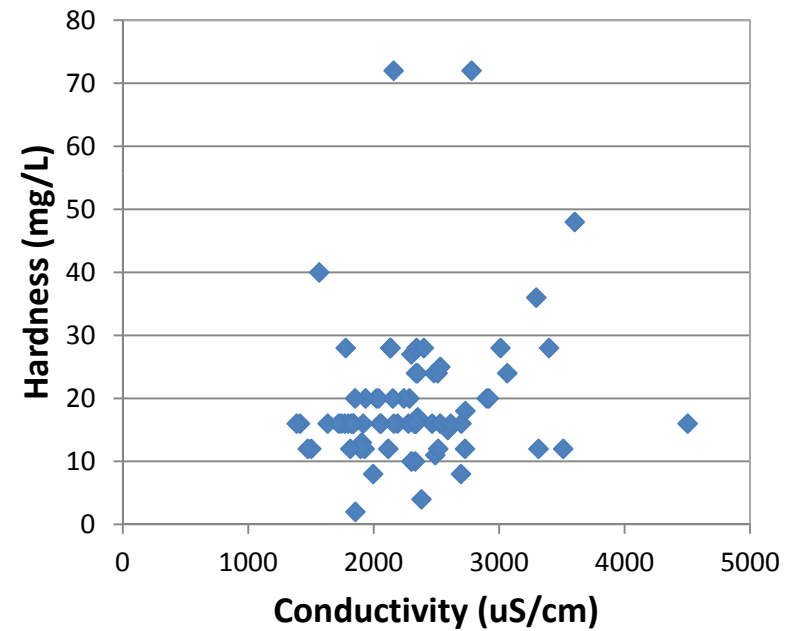
Data from AECOM

4-d *D. magna* method

- 4-d *D. magna* method shows promise as additional / alternative / site-specific test method
 - used in research / TIE studies
 - sensitivity / applicability of method
 - surrogate for *C. dubia* with TDS issues
 - Substitute in certain specific cases?



Example of relationships of
different water quality
Parameters in Raton Basin



ATP Work Plan outline

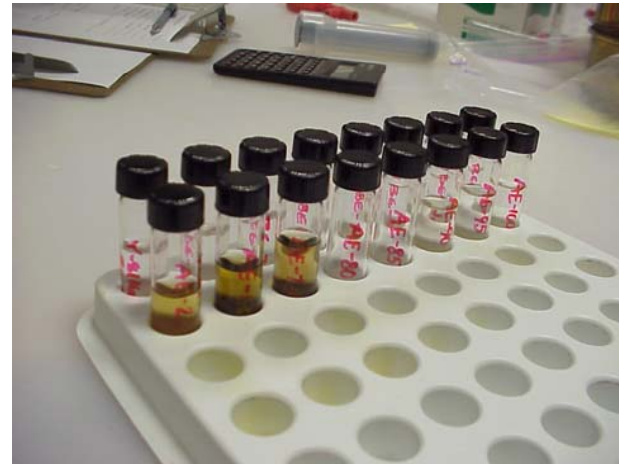
- Meet to discuss the work plan
- Toxicity testing
 - Chronic WET studies
 - Toxicity identification evaluation (Phase I TIE) studies
- Bioassessment Data / Surveys
- Final evaluation & mtgs

ATP Work Plan outline – cont.

- Toxicity testing
 - Chronic WET studies
 - *C. dubia*
 - Fathead minnows
 - *D. magna*
 - Currently performing these studies at outfalls

ATP Work Plan outline – cont.

- Toxicity testing
 - Investigating the cause of toxicity
 - Toxicity identification evaluation (Phase I TIE) studies



MeOH fractions – 2-L SPE elution

Toxicity Identification Evaluation (TIE)

- Series of physico-chemical manipulations designed to target specific types of toxicants to determine cause of toxicity
 - Some identified toxicants
 - Ammonia
 - Total Dissolved Solids (TDS) / Ions
 - OP Pesticides (Diazinon)
 - Carbamate pesticides (Carbaryl)
 - Zinc
 - Copper
 - Surfactants
 - Combination of two or more

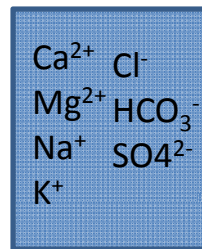
Phase I TIE Test
Baseline Toxicity (unaltered effluent)
pH Adjustment (acidic, neutral, basic)
Aeration (acidic, neutral, basic)
Filtration (acidic, neutral, basic)
Solid-phase extraction (SPE) (acidic, neutral, basic)
EDTA Chelation
Oxidant Reduction (STS)
pH Control (testing under CO ₂ blanket)

Phase I TIE Manipulations

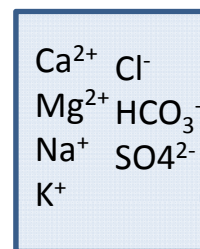
Phase I TIE Test	Toxicants Addressed	Examples
Baseline Toxicity	None (a comparison for other tests)	---
pH Adjustment	Toxicants that degrade under acidic or basic conditions	acidic = cyanide and sulfide basic = malathion
Aeration	Toxicants that are oxidizable, volatile, or sublutable	Surfactants, organic compounds
Filtration	Filterable toxicants	cationic metals under basic conditions
SPE (solid-phase extraction with C ₁₈)	Non-polar organic toxicants	Pesticides, VOC
EDTA Chelation	Some cationic metals	Copper, zinc, nickel
Oxidant Reduction	Oxidants, some cationic metals	Chlorine, peroxide; Copper, cadmium
Graduated pH	pH-sensitive toxicants	Ammonia, many metals, bicarbonate

ATP Work Plan outline – cont.

- Toxicity testing
 - Investigating the cause of toxicity
 - Toxicity identification evaluation (Phase I TIE) studies
 - TDS ion mock studies (Phase III TIE)
 - Match specific ion concentrations in the effluent & perform side-by-side studies (effluent & lab water)



Effluent



TDS Mock (reconstituted lab water)

ATP Work Plan outline – cont.

- Bioassessment Data / Surveys
 - Benthic macroinvertebrate surveys
 - Fish surveys
 - Periphyton surveys
 - Work performed in 2010-2011 by GEI

ATP Work Plan outline

- Would like to received input / feedback on proposed work plan
 - Additional data needs?
 - Prepare work plan
 - Submit work plan for consideration